Supporting Information

Copper-catalyzed aerobic oxygenative cross dehydrogenative coupling of methyl ketones with para-C-H of primary anilines

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A. General information

Melting points were measured using a melting point instrument and are uncorrected. $^1$H NMR and $^{13}$C NMR spectra were recorded on Bruker-AV (400 and 100 MHz, respectively) instrument internally referenced to tetramethysilane (TMS) or chloroform signals. HRMS was carried out on a high-resolution mass spectrometer (LCMS-IT-TOF). TLC was performed using commercially available 100–400 mesh silica gel plates (GF254). All reagents were obtained from commercial suppliers and used without further purification.

B. General procedure for the coupling of methyl ketones and anilines

A 25 mL Schlenk tube was charged with CuI (0.015 mmol, 3 mg), methyl ketone 1 (0.3 mmol), and aniline derivative 2 (0.33 mmol) in DMSO (0.5 mL), and then boron fluoride etherate (0.06mmol, 8 μL) was added. The tube was equipped with an oxygen balloon, and the mixture was heated at 105 °C under magnetic stirring for 14 h. The reaction was then quenched with water, and the mixture was extracted with ethyl acetate (15 mL×3). The combined organic extracts were dried over anhydrous MgSO$_4$, filtered, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc) to afford the corresponding products 3.

C. Characterization data of products

1-(4-aminophenyl)-2-phenylethane-1,2-dione (3aa)

The titled compound was obtained through the general procedure with acetophenone (0.3 mmol, 36 mg), aniline (0.33 mmol, 31 mg). The column chromatography on silica gel (petroleum ether/EtOAc=2/1, R$_f$ = 0.3) afforded 48.5 mg (72% yield) of the product as yellow solid. Mp 124–126 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.95 (d, $J$ = 8.5 Hz, 2H), 7.74 (d, $J$ = 8.7 Hz, 2H), 7.61 (t, $J$ = 7.4 Hz, 1H), 7.46 (t, $J$ = 7.7 Hz, 2H), 6.60 (d, $J$ = 8.8 Hz, 2H), 4.48 (s, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 195.6, 192.7, 153.1, 134.5, 133.4, 132.6, 129.8, 128.8, 122.9, 113.9. HRMS (ESI) for C$_{14}$H$_{11}$NO$_2$: [M+Na]$^+$ 248.0682, found 248.0681.

1-(4-aminophenyl)-2-(4-chlorophenyl)ethane-1,2-dione (3ba)

The titled compound was obtained through the general procedure with 1-(4-chlorophenyl)ethanone
(0.3 mmol, 46 mg), aniline (0.33 mmol, 31 mg). The column chromatography on silica gel (petroleum ether/EtOAc=2/1, Rf = 0.3) afforded 50.5 mg (65% yield) of the product as yellow solid. Mp 154–156 °C. 1H NMR (400 MHz, CDCl₃) δ 7.90 (d, J = 8.5 Hz, 2H), 7.74 (d, J = 8.6 Hz, 2H), 7.44 (d, J = 8.5 Hz, 2H), 6.62 (d, J = 8.5 Hz, 2H), 4.47 (s, 2H). 13C NMR (100 MHz, CDCl₃) δ 194.0, 191.9, 153.1, 141.1, 132.6, 131.8, 131.1, 129.2, 122.7, 113.9. HRMS (ESI) for C₁₄H₁₀ClNO₂: [M+Na]⁺ 282.0292, found 282.0286.

1-(4-aminophenyl)-2-(4-bromophenyl)ethane-1,2-dione (3ca)

The titled compound was obtained through the general procedure with 1-(4-bromophenyl)ethanone (0.3 mmol, 59 mg), aniline (0.33 mmol, 31 mg). The column chromatography on silica gel (petroleum ether/EtOAc=2/1, Rf = 0.3) afforded 42.0 mg (46% yield) of the product as yellow solid. Mp 144–146 °C. 1H NMR (400 MHz, CDCl₃) δ 7.81 (d, J = 8.6 Hz, 2H), 7.73 (d, J = 8.7 Hz, 2H), 7.61 (d, J = 8.6 Hz, 2H), 6.61 (d, J = 8.8 Hz, 2H), 4.48 (s, 2H). 13C NMR (100 MHz, CDCl₃) δ 194.2, 191.9, 153.2, 132.6, 132.2, 132.1, 131.2, 130.0, 122.7, 113.9. HRMS (ESI) for C₁₄H₁₀BrNO₂: [M+Na]⁺ 325.9787, found 325.9780.

1-(4-aminophenyl)-2-(4-iodophenyl)ethane-1,2-dione (3da)

The titled compound was obtained through the general procedure with 1-(4-iodophenyl)ethanone (0.3 mmol, 74 mg), aniline (0.33 mmol, 31 mg). The column chromatography on silica gel (petroleum ether/EtOAc=2/1, Rf = 0.3) afforded 70.3 mg (67% yield) of the product as yellow solid. Mp 128–130 °C. 1H NMR (400 MHz, CDCl₃) δ 7.82 (d, J = 8.5 Hz, 2H), 7.71 (d, J = 8.7 Hz, 2H), 7.64 (d, J = 8.5 Hz, 2H), 6.59 (d, J = 8.8 Hz, 2H), 4.55 (s, 2H). 13C NMR (100 MHz, CDCl₃) δ 194.6, 191.9, 153.3, 138.1, 132.6, 132.2, 132.1, 131.2, 130.0, 122.7, 113.9. HRMS (ESI) for C₁₄H₁₀INO₂: [M+Na]⁺ 373.9648, found 373.9652.

1-(4-aminophenyl)-2-(4-hydroxyphenyl)ethane-1,2-dione (3ea)

The titled compound was obtained through the general procedure with 1-(4-hydroxyphenyl)ethanone (0.3 mmol, 41 mg), aniline (0.33 mmol, 31 mg). The column chromatography on silica gel (petroleum ether/EtOAc=1/2, Rf = 0.25) afforded 33.3 mg (46% yield) of the product as yellow solid. Mp 172–174 °C. 1H NMR (400 MHz, DMSO) δ 10.73 (s, 1H), 7.73 (d, J = 8.8 Hz, 2H), 7.55 (d, J = 8.6 Hz, 2H), 6.92 (d, J = 8.8 Hz, 2H), 6.62 (d, J = 8.9 Hz, 2H), 6.51 (s, 2H). 13C NMR (100 MHz, DMSO) δ 194.4, 192.4, 163.5, 155.5, 132.1, 132.0, 124.7, 120.1, 115.9, 113.0. HRMS (ESI) for C₁₄H₁₁NO₃: [M+Na]⁺ 264.0631, found 264.0633.
1-(4-aminophenyl)-2-(4-methoxyphenyl)ethane-1,2-dione (3fa)

The titled compound was obtained through the general procedure with 1-(4-methoxyphenyl)ethanone (0.3 mmol, 45 mg), aniline (0.33 mmol, 31 mg). The column chromatography on silica gel (petroleum ether/EtOAc=2/1, R_f = 0.2) afforded 45.2 mg (59% yield) of the product as yellow solid. Mp 145–147 °C.

^1H NMR (400 MHz, CDCl_3) δ 7.92 (d, J = 8.7 Hz, 2H), 7.73 (d, J = 8.5 Hz, 2H), 6.93 (d, J = 8.7 Hz, 2H), 6.59 (d, J = 8.5 Hz, 2H), 4.46 (s, 2H), 3.85 (s, 3H).

^13C NMR (100 MHz, CDCl_3) δ 194.2, 193.1, 164.6, 153.0, 132.5, 132.2, 126.5, 123.1, 114.1, 113.8, 55.5. HRMS (ESI) for C_{15}H_{13}NO_3: [M+Na]^+ 278.0788, found 278.0781.

1-(4-aminophenyl)-2-(4-(benzyloxy)phenyl)ethane-1,2-dione (3ga)

The titled compound was obtained through the general procedure with 1-(4-benzyloxyphenyl)ethanone (0.3 mmol, 68 mg), aniline (0.33 mmol, 31 mg). The column chromatography on silica gel (petroleum ether/EtOAc=2/1, R_f = 0.25) afforded 37.9 mg (38% yield) of the product as yellow solid. Mp 164–166 °C.

^1H NMR (400 MHz, CDCl_3) δ 7.93 (d, J = 8.9 Hz, 2H), 7.76 (d, J = 8.7 Hz, 2H), 7.38 (dt, J = 12.8, 7.0 Hz, 5H), 7.02 (d, J = 8.9 Hz, 2H), 6.62 (d, J = 8.8 Hz, 2H), 5.13 (s, 2H), 4.39 (s, 2H).

^13C NMR (100 MHz, CDCl_3) δ 194.1, 193.0, 163.8, 152.8, 135.8, 132.6, 132.3, 128.7, 128.3, 127.4, 126.7, 123.3, 115.0, 113.9, 70.2. HRMS (ESI) for C_{21}H_{17}NO_3: [M+Na]^+ 354.1101, found 354.1097.

1-(4-aminophenyl)-2-(4-(methylthio)phenyl)ethane-1,2-dione (3ha)

The titled compound was obtained through the general procedure with 1-(4-methylthiophenyl)ethanone (0.3 mmol, 50 mg), aniline (0.33 mmol, 31 mg). The column chromatography on silica gel (petroleum ether/EtOAc=2/1, R_f = 0.25) afforded 49.5 mg (61% yield) of the product as yellow solid. Mp 112–114 °C.

^1H NMR (400 MHz, CDCl_3) δ 7.84 (d, J = 8.6 Hz, 2H), 7.74 (d, J = 8.6 Hz, 2H), 7.25 (d, J = 8.7 Hz, 2H), 6.61 (d, J = 8.7 Hz, 2H), 4.47 (s, 2H), 2.49 (s, 3H).

^13C NMR (100 MHz, CDCl_3) δ 194.5, 192.7, 153.0, 148.2, 132.6, 130.1, 129.6, 124.9, 123.0, 113.8, 14.5. HRMS (ESI) for C_{15}H_{13}NO_2S: [M+Na]^+ 294.0559, found 294.0562.

1-(4-aminophenyl)-2-(4-(methylsulfonyl)phenyl)ethane-1,2-dione (3ia)

The titled compound was obtained through the general procedure with 1-(4-methylsulfonylphenyl)ethanone (0.3 mmol, 59 mg), aniline (0.33 mmol, 31 mg). The column chromatography on silica gel (petroleum ether/EtOAc=2/1, R_f = 0.3) afforded 62.6 mg (69% yield) of the product as yellow solid. Mp 112–114 °C.
yellow solid. Mp 156–158 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.11 (d, $J = 8.4$ Hz, 2H), 8.02 (d, $J = 8.4$ Hz, 2H), 6.62 (d, $J = 8.7$ Hz, 2H), 4.61 (s, 2H), 3.06 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 193.4, 190.9, 153.6, 145.0, 137.3, 132.7, 130.6, 127.8, 122.1, 113.9, 44.1. HRMS (ESI) for C$_{15}$H$_{13}$NO$_4$S: [M+Na]$^+$ 326.0457, found 326.0455.

4-(2-(4-aminophenyl)-2-oxoacetyl)benzonitrile (3ja)
The titled compound was obtained through the general procedure with 4-acetylbenzonitrile (0.3 mmol, 44 mg), aniline (0.33 mmol, 31 mg). The reaction was performed for 4 h. The column chromatography on silica gel (petroleum ether/EtOAc=2/1, $R_f = 0.35$) afforded 33.8 mg (45% yield) of the product as yellow solid. Mp 147–149 °C. $^1$H NMR (400 MHz, DMSO) $\delta$ 8.11 – 7.98 (m, 4H), 7.62 (d, $J = 8.6$ Hz, 2H), 6.78 – 6.58 (m, 4H). $^{13}$C NMR (100 MHz, DMSO) $\delta$ 194.5, 190.3, 156.1, 136.0, 133.2, 132.5, 129.8, 119.2, 117.9, 116.5, 113.1. HRMS (ESI) for C$_{15}$H$_{10}$N$_2$O$_2$: [M+Na]$^+$ 273.0634, found 273.0633.

1-(4-aminophenyl)-2-(4-nitrophenyl)ethane-1,2-dione (3ka)
The titled compound was obtained through the general procedure with 1-(4-nitrophenyl)ethanone (0.3 mmol, 49 mg), aniline (0.33 mmol, 31 mg). The column chromatography on silica gel (petroleum ether/EtOAc=2/1, $R_f = 0.25$) afforded 37.3 mg (46% yield) of the product as yellow solid. Mp 172–174 °C. $^1$H NMR (400 MHz, DMSO) $\delta$ 8.40 (d, $J = 8.8$ Hz, 2H), 8.12 (d, $J = 8.8$ Hz, 2H), 7.63 (d, $J = 8.6$ Hz, 2H), 6.80 – 6.57 (m, 4H). $^{13}$C NMR (100 MHz, DMSO) $\delta$ 194.2, 190.1, 156.1, 150.7, 137.4, 132.6, 130.7, 124.3, 119.1, 113.1. HRMS (ESI) for C$_{14}$H$_{10}$N$_2$O$_4$: [M+Na]$^+$ 293.0533, found 293.0538.

1-[[1,1'-biphenyl]-4-yl]-2-(4-aminophenyl)ethane-1,2-dione (3la)
The titled compound was obtained through the general procedure with 1-[[1,1'-biphenyl]-4-yl]ethanone (0.3 mmol, 59 mg), aniline (0.33 mmol, 31 mg). The column chromatography on silica gel (petroleum ether/EtOAc=2/1, $R_f = 0.3$) afforded 45.0 mg (50% yield) of the product as yellow solid. Mp 170–172 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.04 (d, $J = 8.4$ Hz, 2H), 7.80 (d, $J = 8.7$ Hz, 2H), 7.70 (d, $J = 8.5$ Hz, 2H), 7.62 (d, $J = 7.2$ Hz, 2H), 7.47 (t, $J = 7.3$ Hz, 2H), 7.40 (d, $J = 7.2$ Hz, 1H), 6.63 (d, $J = 8.8$ Hz, 2H), 4.45 (s, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 195.1, 192.7, 153.0, 147.1, 139.5, 132.6, 132.1, 130.4, 128.9, 128.5, 127.5, 127.3, 123.0, 113.9. HRMS (ESI) for C$_{20}$H$_{15}$NO$_2$: [M+Na]$^+$ 324.0995, found 324.0991.
The title compound was obtained through the general procedure with 1-(3-methoxyphenyl)ethanone (0.3 mmol, 45 mg), aniline (0.33 mmol, 31 mg). The column chromatography on silica gel (petroleum ether/EtOAc=2/1, R_f=0.3) afforded 61.1 mg (80% yield) of the product as yellow solid. Mp 122–124 °C.

1H NMR (400 MHz, CDCl_3) δ 7.71 (d, J = 8.6 Hz, 2H), 7.51 (s, 1H), 7.46 (d, J = 7.6 Hz, 1H), 7.34 (t, J = 7.9 Hz, 1H), 7.15 (d, J = 8.2 Hz, 1H), 6.59 (d, J = 8.7 Hz, 2H), 4.53 (s, 2H), 3.81 (s, 3H).

13C NMR (100 MHz, CDCl_3) δ 195.5, 192.6, 159.8, 153.2, 134.6, 132.5, 129.8, 123.0, 122.7, 121.3, 113.8, 112.9, 55.4. HRMS (ESI) for C_{15}H_{13}NO_3: [M+Na]^+ 278.0788, found 278.0792.

The title compound was obtained through the general procedure with N-(3-acetylphenyl)acetamide (0.3 mmol, 53 mg), aniline (0.33 mmol, 31 mg). The column chromatography on silica gel (petroleum ether/EtOAc=1/1, R_f=0.2) afforded 43.2 mg (51% yield) of the product as yellow solid. Mp 176–178 °C.

1H NMR (400 MHz, DMSO) δ 10.23 (s, 1H), 8.14 (s, 1H), 7.98 (d, J = 7.0 Hz, 1H), 7.60 (d, J = 8.4 Hz, 2H), 7.57 – 7.49 (m, 2H), 6.67 (d, J = 8.7 Hz, 2H), 6.61 (s, 2H), 2.07 (s, 3H).

13C NMR (100 MHz, DMSO) δ 195.9, 191.7, 168.7, 155.8, 140.0, 133.6, 132.2, 129.7, 124.9, 123.7, 119.7, 119.3, 113.1, 23.9. HRMS (ESI) for C_{16}H_{14}N_2O_3: [M+Na]^+ 305.0897, found 305.0897.

The title compound was obtained through the general procedure with 1-(2-methoxyphenyl)ethanone (0.3 mmol, 45 mg), aniline (0.33 mmol, 31 mg). The column chromatography on silica gel (petroleum ether/EtOAc=2/1, R_f=0.3) afforded 45.1 mg (59% yield) of the product as yellow solid. Mp 141–143 °C.

1H NMR (400 MHz, CDCl_3) δ 7.98 (dd, J = 7.8, 1.6 Hz, 1H), 7.72 (d, J = 8.6 Hz, 2H), 7.56 (t, J = 7.6 Hz, 1H), 7.09 (t, J = 7.3 Hz, 2H), 6.92 (d, J = 8.5 Hz, 2H), 6.62 (d, J = 8.6 Hz, 2H), 4.30 (s, 2H), 3.59 (s, 3H). 13C NMR (100 MHz, CDCl_3) δ 195.2, 192.2, 160.3, 152.0, 136.0, 131.9, 130.7, 124.2, 122.9, 121.3, 113.9, 112.4, 55.7. HRMS (ESI) for C_{15}H_{13}NO_3: [M+Na]^+ 278.0788, found 278.0795.

The title compound was obtained through the general procedure with 1-(3,4-dimethylphenyl)ethanone (0.3 mmol, 45 mg), aniline (0.33 mmol, 31 mg). The column chromatography on silica gel (petroleum ether/EtOAc=2/1, R_f=0.3) afforded 45.1 mg (59% yield) of the product as yellow solid. Mp 141–143 °C.
phenyl)ethanone (0.3 mmol, 44 mg), aniline (0.33 mmol, 31 mg). The column chromatography on silica gel (petroleum ether/EtOAc=2/1, R<sub>f</sub> = 0.3) afforded 51.6 mg (68% yield) of the product as yellow solid. Mp 132–134 °C. ¹H NMR (400 MHz, DMSO) δ 7.66 – 7.52 (m, 4H), 7.35 (d, J = 7.9 Hz, 1H), 6.64 (dd, J = 8.6, 3.9 Hz, 2H), 6.56 (s, 2H), 2.31 (s, 3H), 2.28 (s, 3H). ¹³C NMR (100 MHz, DMSO) δ 195.8, 192.0, 155.6, 144.6, 143.5, 132.1, 131.0, 130.2, 129.8, 127.2, 119.8, 113.0, 19.8, 19.2. HRMS (ESI) for C<sub>16</sub>H<sub>15</sub>NO<sub>2</sub>: [M+Na]<sup>+</sup> 276.0995, found 276.0996.

1-(4-aminophenyl)-2-(naphthalen-1-yl)ethane-1,2-dione (3qa)
The titled compound was obtained through the general procedure with 1-(naphthalen-1-yl)ethanone (0.3 mmol, 51 mg), aniline (0.33 mmol, 31 mg). The column chromatography on silica gel (petroleum ether/EtOAc=2/1, R<sub>f</sub> = 0.3) afforded 42.7 mg (52% yield) of the product as yellow solid. Mp 138–140 °C. ¹H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.28 (d, J = 8.7 Hz, 1H), 8.07 (d, J = 8.2 Hz, 1H), 7.96 – 7.88 (m, 2H), 7.80 (d, J = 8.6 Hz, 2H), 7.74 – 7.067 (m, 1H), 7.62 – 7.57 (m, 1H), 7.45 (d, J = 8.0 Hz, 1H), 6.60 (d, J = 8.7 Hz, 2H), 4.41 (s, 2H). ¹³C NMR (100 MHz, CDCl<sub>3</sub>) δ 198.1, 192.9, 152.8, 135.5, 134.8, 134.0, 132.7, 130.9, 129.1, 128.7, 126.9, 125.9, 124.4, 123.3, 113.9. HRMS (ESI) for C<sub>18</sub>H<sub>13</sub>NO<sub>2</sub>: [M+Na]<sup>+</sup> 298.0838, found 298.0837.

1-(4-aminophenyl)-2-(naphthalen-2-yl)ethane-1,2-dione (3ra)
The titled compound was obtained through the general procedure with 1-(naphthalen-2-yl)ethanone (0.3 mmol, 51 mg), aniline (0.33 mmol, 31 mg). The column chromatography on silica gel (petroleum ether/EtOAc=2/1, R<sub>f</sub> = 0.3) afforded 35.5 mg (43% yield) of the product as yellow solid. Mp 147–149 °C. ¹H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.42 (s, 1H), 8.08 (dd, J = 8.6, 1.7 Hz, 1H), 7.92 (d, J = 8.6 Hz, 1H), 7.90 – 7.84 (m, 2H), 7.80 (d, J = 8.6 Hz, 2H), 7.60 (t, J = 7.7 Hz, 1H), 7.51 (t, J = 7.5 Hz, 1H), 6.60 (d, J = 8.8 Hz, 2H), 4.49 (s, 2H). ¹³C NMR (100 MHz, CDCl<sub>3</sub>) δ 195.6, 192.8, 153.1, 136.1, 133.3, 132.6, 132.3, 130.7, 129.8, 129.2, 128.9, 127.8, 126.9, 123.7, 122.9, 113.8. HRMS (ESI) for C<sub>18</sub>H<sub>13</sub>NO<sub>2</sub>: [M+Na]<sup>+</sup> 298.0838, found 298.0837.

1-(4-aminophenyl)-2-(thiophen-2-yl)ethane-1,2-dione (3sa)
The titled compound was obtained through the general procedure with 1-(thiophen-2-yl)ethanone (0.3 mmol, 38 mg), aniline (0.33 mmol, 31 mg). The column chromatography on silica gel (petroleum ether/EtOAc=2/1, R<sub>f</sub> = 0.3) afforded 39.4 mg (57% yield) of the product as yellow solid. Mp 94–96 °C. ¹H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.84 (d, J = 8.7 Hz, 2H), 7.80 – 7.74 (m, 2H), 7.15 (t, J = 4.4 Hz, 1H), 6.63 (d, J = 8.7 Hz, 2H), 4.43 (s, 2H). ¹³C NMR (100 MHz, CDCl<sub>3</sub>) δ 190.2, 186.8, 153.0, 140.4, 136.4, 136.2, 133.0, 128.6, 122.6, 113.9. HRMS (ESI) for C<sub>12</sub>H<sub>9</sub>NO<sub>2</sub>S: [M+Na]<sup>+</sup> 254.0246, found 254.0247.
1-(4-aminophenyl)-2-cyclopropylethane-1,2-dione (3ta)
The titled compound was obtained through the general procedure with 1-cyclopropylethanone (0.3 mmol, 25 mg), aniline (0.33 mmol, 31 mg). The column chromatography on silica gel (petroleum ether/EtOAc=2/1, R_f = 0.35) afforded 20.0 mg (35% yield) of the product as yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.83 (d, J = 8.7 Hz, 2H), 6.64 (d, J = 8.7 Hz, 2H), 4.33 (s, 2H), 2.53 – 2.41 (m, 1H), 1.33 – 1.24 (m, 2H), 1.18 – 1.07 (m, 2H). ^13C NMR (100 MHz, CDCl_3) δ 203.9, 190.8, 152.6, 133.0, 122.2, 113.9, 18.8, 12.8. HRMS (ESI) for C_{11}H_{11}NO_2: [M+Na]^+ 212.0682, found 212.0679.

1-(4-amino-3-fluorophenyl)-2-phenylethane-1,2-dione (3ab)
The titled compound was obtained through the general procedure with acetophenone (0.3 mmol, 36 mg), 2-fluoroaniline (0.33 mmol, 37 mg). The column chromatography on silica gel (petroleum ether/EtOAc=2/1, R_f = 0.3) afforded 56.8 mg (78% yield) of the product as yellow solid. Mp 114–116 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.94 (d, J = 7.2 Hz, 2H), 7.66 – 7.56 (m, 2H), 7.48 (dd, J = 15.6, 7.8 Hz, 3H), 6.71 (t, J = 8.4 Hz, 1H), 4.59 (s, 2H). ^13C NMR (100 MHz, CDCl_3) δ 194.8, 192.1, 149.1, 134.7, 133.1, 129.8, 128.9, 128.5, 122.9, 116.0, 115.1. HRMS (ESI) for C_{14}H_{10}FNO_2: [M+Na]^+ 266.0588, found 266.0580.

1-(4-amino-3-chlorophenyl)-2-phenylethane-1,2-dione (3ac)
The titled compound was obtained through the general procedure with acetophenone (0.3 mmol, 36 mg), 2-chloroaniline (0.33 mmol, 42 mg). The column chromatography on silica gel (petroleum ether/EtOAc=2/1, R_f = 0.3) afforded 59.7 mg (77% yield) of the product as yellow solid. Mp 129–131 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.94 (d, J = 7.2 Hz, 2H), 7.66 – 7.58 (m, 2H), 7.47 (t, J = 7.8 Hz, 2H), 6.71 (d, J = 8.5 Hz, 1H), 4.92 (s, 2H). ^13C NMR (100 MHz, CDCl_3) δ 194.7, 191.8, 145.8, 135.3, 134.8, 133.0, 131.6, 130.5, 129.8, 128.9, 123.4, 118.5, 114.5. HRMS (ESI) for C_{14}H_{10}ClNO_2: [M+Na]^+ 282.0292, found 282.0289.

1-(4-amino-3-(trifluoromethoxy)phenyl)-2-phenylethane-1,2-dione (3ad)
The titled compound was obtained through the general procedure with acetophenone (0.3 mmol, 36 mg), 2-(trifluoromethoxy)aniline (0.33 mmol, 58 mg). The column chromatography on silica gel (petroleum ether/EtOAc=2/1, R_f = 0.3) afforded 69.4 mg (75% yield) of the product as yellow solid. Mp 130–132 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.95 (d, J = 8.4 Hz, 2H), 7.83 (s, 1H), 7.64 – 7.57 (m, 2H), 7.48 (t, J = 7.7 Hz, 2H), 6.74 (d, J = 8.5 Hz, 1H), 4.79 (s, 2H). ^13C NMR (100 MHz, CDCl_3) δ 194.7, 191.8, 149.1, 134.7, 133.0, 131.6, 130.5, 129.8, 128.9, 123.4, 118.5, 115.3. HRMS (ESI) for C_{15}H_{10}ClF_3NO_3: [M+Na]^+ 332.0505, found 332.0511.
1-(6-amino-[1,1'-biphenyl]-3-yl)-2-phenylethane-1,2-dione (3ae)

The titled compound was obtained through the general procedure with acetophenone (0.3 mmol, 36 mg), [1,1'-biphenyl]-2-amine (0.33 mmol, 56 mg). The column chromatography on silica gel (petroleum ether/EtOAc=2/1, R_f = 0.35) afforded 40.7 mg (45% yield) of the product as yellow solid. Mp 155–157 °C. 

1H NMR (400 MHz, CDCl₃) δ 7.98 (d, J = 7.2 Hz, 2H), 7.83 – 7.72 (m, 2H), 7.62 (t, J = 7.5 Hz, 1H), 7.51 – 7.36 (m, 7H), 6.75 (d, J = 8.4 Hz, 1H), 4.49 (s, 2H).

13C NMR (100 MHz, CDCl₃) δ 195.3, 192.8, 150.2, 137.5, 134.5, 133.4, 133.1, 131.5, 129.9, 129.1, 128.9, 128.8, 127.9, 126.7, 123.4, 114.6. HRMS (ESI) for C₂₀H₁₅NO₂: [M+Na]^+ 324.0995, found 324.0989.

1-(4-amino-3-methylphenyl)-2-phenylethane-1,2-dione (3af)

The titled compound was obtained through the general procedure with acetophenone (0.3 mmol, 36 mg), o-toluidine (0.33 mmol, 35 mg). The column chromatography on silica gel (petroleum ether/EtOAc=2/1, R_f = 0.3) afforded 51.5 mg (72% yield) of the product as yellow solid. Mp 123–125 °C. 

1H NMR (400 MHz, CDCl₃) δ 7.96 (d, J = 7.2 Hz, 2H), 7.68 (s, 1H), 7.67 – 7.56 (m, 2H), 7.48 (t, J = 7.7 Hz, 2H), 6.63 (d, J = 8.3 Hz, 1H), 4.35 (s, 2H), 2.14 (s, 3H).

13C NMR (100 MHz, CDCl₃) δ 195.5, 193.0, 151.4, 134.4, 133.5, 132.8, 130.6, 129.8, 123.1, 121.3, 113.7, 17.0. HRMS (ESI) for C₁₅H₁₃NO₂: [M+Na]^+ 262.0838, found 262.0839.

1-(4-amino-3-methoxyphenyl)-2-phenylethane-1,2-dione (3ag)

The titled compound was obtained through the general procedure with acetophenone (0.3 mmol, 36 mg), 2-methoxyaniline (0.33 mmol, 41 mg). The column chromatography on silica gel (petroleum ether/EtOAc=2/1, R_f = 0.25) afforded 38.4 mg (50% yield) of the product as yellow solid. Mp 135–137 °C. 

1H NMR (400 MHz, CDCl₃) δ 7.97 (d, J = 7.1 Hz, 2H), 7.62 (d, J = 7.2 Hz, 2H), 7.67 – 7.56 (m, 2H), 7.48 (t, J = 7.7 Hz, 2H), 6.62 (d, J = 8.2 Hz, 1H), 4.34 (d, J = 167.0 Hz, 2H), 3.92 (s, 3H).

13C NMR (100 MHz, CDCl₃) δ 195.3, 192.9, 146.6, 143.8, 134.4, 133.5, 132.8, 130.6, 129.8, 123.1, 121.3, 113.7, 55.7. HRMS (ESI) for C₁₅H₁₃NO₃: [M+Na]^+ 278.0788, found 278.0793.

1-(4-amino-2-fluorophenyl)-2-phenylethane-1,2-dione (3ah)

The titled compound was obtained through the general procedure with acetophenone (0.3 mmol, 36 mg), 3-fluoroaniline (0.33 mmol, 37 mg). The column chromatography on silica gel (petroleum ether/EtOAc=2/1, R_f = 0.3) afforded 43.7 mg (60% yield) of the product as yellow solid. Mp 117–
119 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.92 (d, $J = 8.2$ Hz, 2H), 7.86 − 7.76 (m, 1H), 7.61 (t, $J = 7.4$ Hz, 1H), 7.47 (t, $J = 7.7$ Hz, 2H), 6.45 (dd, $J = 8.7, 2.1$ Hz, 1H), 6.18 (dd, $J = 13.0, 2.1$ Hz, 1H), 4.67 (s, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 194.5, 190.5, 165.3, 155.4, 134.3, 132.5, 132.4, 129.6, 128.8, 111.7, 111.0, 100.1. HRMS (ESI) for C$_{14}$H$_{10}$FNO$_2$: [M+Na]$^+$ 266.0588, found 266.0587.

1-(4-aminophenyl)-2-phenylethane-1,2-diol (7)

Reaction conditions: 3aa (0.2 mmol), NaBH$_4$ (2 equiv), H$_2$O (2 equiv), THF (0.2 M), reflux, 0.5 h. The column chromatography on silica gel (petroleum ether/EtOAc=1/1, $R_f = 0.3$) afforded 38.8 mg (85% yield) of the product as light yellow solid (dr = 10:1, determined by NMR). Mp 192–194 °C. $^1$H NMR of the main isomer (400 MHz, d$_6$-DMSO) $\delta$ 7.25–7.10 (m, 5H), 6.88 (d, $J = 8.0$ Hz, 2H), 6.43 (d, $J = 8.0$ Hz, 2H), 5.00 (d, $J = 4.8$ Hz, 1H), 4.85 (d, $J = 4.8$ Hz, 1H), 4.85 (br, 2H), 4.93 (t, $J = 4.8$ Hz, 1H) 4.39, (t, $J = 4.8$ Hz, 1H); $^{13}$C NMR of the main isomer (100 MHz, d$_6$-DMSO) $\delta$ 147.2, 143.6, 130.4, 129.0, 127.4, 127.1, 126.4, 113.0, 77.2, 76.9. HRMS (ESI) for C$_{14}$H$_{15}$NO$_2$: [M+H]$^+$ 230.1176, found 230.1178.

4-(3-phenylquinoxalin-2-yl)aniline (8)

Reaction conditions: 3aa (0.2 mmol), benzene-1,2-diamine (1.2 equiv), FeCl$_3$ (2 equiv), EtOH (0.2 M), 65 °C, 12 h. The column chromatography on silica gel (petroleum ether/EtOAc=3/1, $R_f = 0.5$) afforded 44.0 mg (74% yield) of the product as yellow solid. Mp 215–217 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.15–8.12 (m, 2H), 7.76–7.69 (m, 2H), 7.58–7.55 (m, 2H), 7.37–7.34 (m, 5H), 6.60 (d, $J = 8.4$ Hz, 2H), 3.81 (s, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 153.4, 153.3, 147.2, 141.3, 140.7, 139.6, 131.3, 129.7, 129.6, 129.2, 129.0, 128.9, 128.8, 128.6, 128.2, 114.5. HRMS (ESI) for C$_{20}$H$_{15}$N$_3$: [M+H]$^+$ 298.1339, found 298.1344.

D. $^1$H NMR and $^{13}$C NMR spectra of all products
$^1$H NMR and $^{13}$C NMR spectra of 3aa

$^1$H NMR and $^{13}$C NMR spectra of 3ba
$^1$H NMR and $^{13}$C NMR spectra of 3ca

S12
\[^{1}\text{H NMR and } ^{13}\text{C NMR spectra of 3da}\]
$^1$H NMR and $^{13}$C NMR spectra of 3ea
$^1$H NMR and $^{13}$C NMR spectra of 3fa
$^1$H NMR and $^{13}$C NMR spectra of 3ga
$^{1}$H NMR and $^{13}$C NMR spectra of 3ha
$^1$H NMR and $^{13}$C NMR spectra of 3ia
\textsuperscript{1}H NMR and \textsuperscript{13}C NMR spectra of 3ja
$^1$H NMR and $^{13}$C NMR spectra of 3ka
$^{1}$H NMR and $^{13}$C NMR spectra of 3la
$^1$H NMR and $^{13}$C NMR spectra of 3ma
$^{1}$H NMR and $^{13}$C NMR spectra of 3na

![Chemical Structure](image)

$^{1}$H NMR and $^{13}$C NMR spectra of 3oa
$^1$H NMR and $^{13}$C NMR spectra of 3pa
$^1$H NMR and $^{13}$C NMR spectra of 3qa
$^1$H NMR and $^{13}$C NMR spectra of 3ra

$^1$H NMR and $^{13}$C NMR spectra of 3sa
$^1$H NMR and $^{13}$C NMR spectra of 3ta
$^1$H NMR and $^{13}$C NMR spectra of 3ab

![Chemical structure](attachment:image.png)

$^1$H NMR and $^{13}$C NMR spectra of 3ac
$^1$H NMR and $^{13}$C NMR spectra of 3ad
1H NMR and 13C NMR spectra of 3ae

1H NMR and 13C NMR spectra of 3af
$^1$H NMR and $^{13}$C NMR spectra of 3ag
$^1$H NMR and $^{13}$C NMR spectra of 3ah
$^1$H NMR and $^{13}$C NMR spectra of 7

![NMR spectra of 7](image)

$^1$H NMR and $^{13}$C NMR spectra of 8